

**An approach to quantify sources, seasonal change, and
biogeochemical processes affecting metal loading to
facilitate decisions for remediation of mine drainage**

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Abstract

Historical mining has left complex problems for remediation in catchments throughout the world. Land managers are faced with the task of making plans for remediation that provide the most benefit to streams, and yet are cost-effective. Remediation plans are facilitated by mass-loading studies that provide detailed spatial profiles of metal loading to the stream to indicate the principal locations of metal loading to the stream, the impact of seasonal changes, and the extent of biogeochemical processes. Three field-scale experiments in the Animas River, near Silverton, Colo., illustrate how this can be accomplished. Each experiment was based on tracer-dilution to estimate discharge along a study reach and synoptic sampling of stream and inflow chemistry. Together, the discharge and chemistry quantify metal loading. A low-flow experiment indicated that sulfate was principally derived from sources upstream from the study area, but that metal loading occurred at three principal locations along the study reach. The experiment included ultrafiltration to define dissolved and colloidal concentrations of metals. Aluminum, copper, and iron were transported principally in the colloidal load. During high-flow conditions of snowmelt runoff, a Lagrangian sampling experiment provided data to interpret changes in loading that can occur seasonally. Although the same locations that were important at low-flow continued to provide loading to the stream, the Lagrangian sampling indicated those locations where snowmelt runoff flushed metals to the stream. Comparison of metal concentrations between the low- and high-flow experiments indicated substantial increases in metal loading at high flow, but little change in metal concentrations. Thus, toxicity resulting from metal concentrations was not substantially greater during snowmelt runoff. Also during high-flow conditions, a detailed temporal sampling at fixed sites provided data about biogeochemical processes that affect metals. The concentration of zinc more than doubled during the diel cycle. Thus, monitoring programs must account for diel variation to provide meaningful results. These experiments indicate how mass-loading experiments provide different kinds of answers that unite to support science-based decisions.

Introduction

Many years of historical mining in the Silverton, Colorado area have left mining wastes that contribute to metal loads to the Animas River. This is typical of hundreds of catchments affected by mining throughout the world, and leaves land managers with difficult decisions about remediation in very complex systems where a single catchment may contain many potential sources of metals to a stream. Land managers must have reliable scientific information to support their decisions. To meet some of these needs, the U.S. Geological Survey has developed a mass-loading approach that focuses on metal loading in a stream through developing detailed spatial profiles of stream discharge and chemistry. The mass-loading approach has had many applications, including the study of hydrologic characteristics of streams (Bencala, McKnight, and Zellweger, 1990;Gooseff et al., 2005a;Gooseff et al., 2005b;Zellweger, 1994), determining the mass loading of metals and other constituents (Boughton, 2001;Broshears et al., 1993;Kimball et al., 2006;Kimball et al., 2002;Nimick and Cleasby, 2001;Wirt et al., 2001), the estimation of pre-mining chemistry of watersheds(Runkel et al., 2007), and quantification of reactive processes in the environment(Harvey and Fuller, 1998;Kimball et al., 1994;Runkel et al., 1996a;Runkel et al., 1996b).

In general, the approach is based on two well-established techniques: the tracer-dilution method (Bencala, McKnight, and Zellweger, 1990) and synoptic sampling (Bencala and McKnight, 1987). The tracer-dilution method provides estimates of stream discharge that are, in turn, used to quantify the amount of water entering the stream in a given stream segment through both tributary and ground-water inflow. Synoptic sampling of stream and inflow chemistry provides a spatially detailed ‘snapshot’ of stream water quality and the inflows that influence changes in the stream. When combined, these techniques provide quantities of loading and mass change to support the different applications.

Mass-loading studies in the Animas River basin (Church, von Guerard, and Finger, 2007;Kimball et al., 2002;Kimball, Walton-Day, and Runkel, 2007) have provided detailed information

about the locations of metal loading to a stream during low-flow conditions. This is the time of year when mine drainage is the least diluted and can be most harmful to aquatic organisms (Besser and Leib, 1999). During low-flow conditions, the longitudinal profile of the stream chemistry might best be considered a steady-state profile, meaning that changes along the study reach are a result of constant sources to the stream and that processes affecting solutes that occur at constant rates. Thus, low-flow conditions permit the evaluation of the relative contribution of many sources and their impact on the stream.

Application of the mass-loading approach to high-flow conditions could provide valuable information on seasonal or transient sources of metals that may increase toxicity. To apply the mass-loading approach during high-flow conditions means that a steady-state condition no longer applies; the longitudinal profile of stream chemistry will vary temporally. To study spatial changes along a study reach when temporal variation occurs requires a different approach. Two possible approaches have been used in this study. First an approach referred to as Lagrangian sampling attempts to follow a parcel of water along the study reach, sampling as the parcel is sequentially affected by inflows and instream processes. The approach has been used for studies of large rivers (Meade and Stevens, Jr., 2007; Moody, 1993), and requires a precise timing of the water movement along the study reach to prepare a sampling schedule that follows the parcel downstream. A second approach involves temporal sampling at fixed locations. With multiple samples at fixed sites, the changes over time at individual sites and from site to site can be determined. This approach can be much more sample-intensive than the Lagrangian sampling.

To evaluate these approaches for low- and high-flow conditions, two field experiments were designed. The first was in August 2002, which was a period of extreme low flow for the Animas River. The second was in April 2003, which was a period when relatively low altitude snowmelt was entering the Animas River. Both experiments were along a study reach of the Animas River between Arrastra

Creek and Silverton (Figure 1), and evaluated the concentrations of many dissolved and colloidal metals. This illustration will focus on the results for pH, SO₄, Fe, Cu, Mn, and Zn. The field experiments will show how the mass-loading approach can help support remediation decisions in three ways. First, it provides quantitative comparisons among the locations of metal loading along a study reach. Second, it quantifies seasonal variation that may affect decisions when mass-loading profiles are compared between low- and high-flow conditions. Third, it quantifies important biogeochemical processes that affect the transport of metals and that should be considered in designing monitoring programs.

Figure 1. Location of study reach and principal sampling sites along the Animas River, August 2002 and April 2003.

Experimental

An initial field-scale experiment that included the current study reach was conducted in August 1997. At that time, discharge of the Animas River at Silverton was 2,260 L/s, and it was a period of monsoon runoff for the Animas River (Paschke, Kimball, and Runkel, 2005). In contrast, discharge during the experiment conducted in August 2002 was 807 L/s, only 38 percent of the flow in 1997. August 2002 was a period of extreme low flow, the fourth year of drought in the Silverton area. Sampling sites from 1997 from a point upstream from Arrastra Creek to Silverton were resampled in 2002, with additional sites located where inflows in the exposed streambed could be sampled because of the low stage of the river. A list of the sampling sites is given in table 1. In April 2003, two field experiments were conducted that included temporal sampling using a Lagrangian design and also the collection of samples for about 28 hours at 6 stream sites by using auto samplers. The discharge in April 2003 was 1,810 L/s. Although the discharge was smaller than the August 1997 base-flow discharge, the goal of the 2003 study was to capture the early season snowmelt runoff from relatively low altitude parts of the upper Animas River Basin. Had the goal been to capture peak flow from high-altitude

snowmelt runoff, the study would have been conducted later in the spring. The methods described for April 2003, however, apply for periods of higher discharge also.

Table 1. Source, downstream distance, site description, low and high-flow discharge and bromide concentration for sites along the Animas River, August 2002 and April 2003.

For either a low- or high-flow application, each stream site represents the downstream end of a stream segment, and the stream segments divide the watershed into increments to account for instream and inflow loads. During high-flow conditions, fewer stream sites can be sampled, so the level of detail between low-flow and high-flow synoptic sampling differs substantially. But for either approach, changes in stream chemistry and discharge between stream sampling sites reflect a net metal load for specific segments. Specific sources that are responsible for the loading within particular stream segments, however, cannot always be identified at this stream reach scale.

Calculation of discharge was based on dilution of the Br tracer along the longitudinal profile of the study reach (Figure 2). Description of the equation for discharge is in the supplementary information. At low flow in 2002, concentrations of Br in samples of inflow waters were near the lower limit of detection of Br except in a few samples that likely had some stream water mixed in. The steady decrease of Br along the study reach provides a clear indication of the gaining reach of the Animas River. The greatest increase occurred from the inflow of Arrastra Creek and from several visible springs from Arrastra Creek to 5,448 m, downstream from the Apsen Mine inflow. From that point to the end of the study reach the gain in stream flow was much smaller, but was measurable. The discharge profile indicates the substantial number of sampling sites that were accessible at low flow (Figure 2A).

Figure 2. Variation of bromide concentration and calculated discharge with distance along the study reach for (A) low flow in August 2002 and (b) high flow in April 2003.

For high flow, fewer sampling sites were selected because of the logistic demands of following a parcel of water downstream (Figure 2B). To prepare a schedule for sampling along the study reach during high-flow conditions, a dye tracer was added to the stream to observe its arrival at the

downstream sampling points. For the April 2003 sampling, we added a dye in the morning, determined the arrival time at the 6 downstream sites with a portable fluorometer, and then used that schedule for the synoptic sampling in the afternoon when snowmelt runoff would affect the stream. Under higher flow conditions, it would be necessary to place stream sampling sites near bridges and at locations where it would be safe to wade the stream. For the high-flow synoptic, 8 stream sampling sites were sampled, compared to 26 sites at low flow. Possible inflow sampling sites, in contrast, were more numerous at high flow because of overland snowmelt runoff to the stream, but logically not all this water could be sampled. Major inflows from the low-flow study were resampled (Table 1), but the effects of snowmelt runoff mostly were tracked by instream changes. Similar to low-flow discharge, an increase in stream discharge occurred at Arrastra Creek, but that increase was only a part of the larger increase that occurred along the rest of the study reach. The contrast between low and high flow were indicated by Br concentration profiles from the tracer injection that clearly reflected the influence of inflow from snowmelt runoff.

The spatial distribution of metal sources is characterized by synoptic sampling, but the method of collecting the synoptic samples differs between low and high flow conditions. For low-flow, steady-state conditions are assumed. Under ideal conditions, samples at all of the sampling sites would be collected simultaneously, providing a description of stream-water quality at that steady state. Personnel limitations generally preclude simultaneous sample collection for so many sites, but the low-flow synoptic study provides an approximate means of describing steady-state conditions by collecting samples over a relatively short time (less than 8 hours) such that the effects of diurnal flow variation are minimized. Sampling for low-flow conditions begins at the downstream end of the study reach and ends upstream of the tracer-injection site. This downstream-to-upstream sampling order is followed in order to avoid disturbing streambed materials so that colloidal concentrations of metals can be determined. Inflow sites that were considered well mixed were sampled using grab techniques. Stream sites that are

not well mixed or where ground-water inflow may be expected were sampled by equal width integration (Ward and Harr, 1990).

High-flow conditions usually are transient and a steady-state assumption is not valid. To accommodate the transient conditions, the synoptic sample must follow the changes within a parcel of water as it flows through the study reach, a so-called Lagrangian sampling scheme (Meade and Stevens, Jr., 2007; Moody, 1993). With the sequence of arrivals times for downstream sites, the synoptic sampling can proceed from upstream to downstream according to the scheduled arrival times, following the parcel of water. As the parcel is sampled, changes in tracer concentration account for increases in discharge, and changes in the chemistry of the water account for effects of inflows and the chemical and biological processes that occur during transport downstream.

Use of two filtration techniques provides three different operationally defined concentrations for each metal. Metal concentration from the unfiltered sample (RA) is a measure of the total-recoverable concentration (dissolved + colloidal), and the ultrafiltrate concentration (UFA) is a measure of the dissolved metal concentration. Colloidal metal concentrations are defined here as the difference between the total-recoverable (RA) and the ultrafiltrate metal concentrations (UFA) for stream samples (Kimball and others, 1995). For the high-flow synoptic, the colloidal concentration was calculated as the difference between the RA and FA samples. The 0.45- μm concentration (FA) measures both the dissolved and the colloidal concentrations that will pass through the 0.45- μm filter. Thus, the FA concentration may not represent truly dissolved concentrations. Aquatic standards for toxicity generally are based on 0.45- μm filtration. The calculation of instream load uses the total-recoverable (RA) concentration because both dissolved and colloidal contributions can be added by inflows.

Data from the 1997 study are published in Church et al. (Church, von Guerard, and Finger, 2007). Data and equations used to prepare loading profiles and to evaluate chemical character for low-

and high-flow synoptic samples and the temporal sequence of samples from auto-samplers during the high-flow synoptic are included in the supplementary information.

Results and Discussion

Quantifying Sources During Low-Flow Conditions

Some of the most important information needed to make decisions about remediation of mine drainage is a basic understand of the location, quantity, and chemical character of metal loading to a stream. Many studies have presented detailed chemical sampling as an approach to evaluate mine sites and to study biogeochemical processes. Our approach also includes detailed sampling of stream and inflow chemistry but all within the context of catchment hydrology. Using this hydrologic context, we are able to evaluate and compare sources of metal loading by using spatially detailed mass-loading profiles. This detailed approach generally is used during low-flow conditions when inflows to the stream, both from surface and ground water, are most likely to be detected. This approach is demonstrated here with the low-flow field experiment from August 2002. First, the role of inflow and stream chemical character in understanding mass-loading profiles is illustrated. The complete chemical analysis of samples from both the low- and high-flow synoptic studies is listed in table S1 (with supplemental material).

Table S1. Chemical analyses of samples from low- and high-flow synoptic studies, Animas River from Arrastra Creek to Silverton, August 2002 and April 2003.

Chemical Character of Inflow Samples

Chemical compositions of inflow samples in a synoptic study provide a framework to understand the possible sources of loading and also the chemical changes along the study reach. Typically, a low-flow study can indicate substantial differences in chemical character among inflow samples that can be related to the various sources of solutes. This was particularly true in August 2002

because of the extreme low-flow conditions. Several inflows that had been covered by stream water at a higher stage of the river were available for sampling. Sampling during snowmelt runoff cannot provide the same level of detail because some inflows are covered physically by the higher stage of the river or because inflows may be diluted by snowmelt. Thus, information on the nature of inflows during high-flow conditions often must come from following the instream chemical changes.

Application of cluster analysis to the low-flow data set distinguished five groups of inflow samples, and their chemical variation is indicated by representative samples for each group (Table 2). Characteristics of these groups reflect a continuum of interaction with mine wastes, and present a complete range from “unaffected” (inflow group 1) to “most affected” (inflow group IV). These groups would appear to accomplish the goal of sampling inflows that are representative of all the types of water affecting the stream. Cluster analysis also identified one inflow sample to be unique (inflow group V). This sample was the only sample affected by weathering a mineralized vein and not by mine wastes. Thus, the sample provides a contrast of impact from un-mined mineralization versus impact from mine wastes, most notably because of its low pH at 2.42 but lower SO₄ than the most affected inflows.

Table 2. Chemical composition of samples representing inflow groups defined by cluster analysis, Animas River, August 2002.

Three views of chemical variability among inflows help to describe the distinctions among these groups and their impact on the Animas River along the study reach. First, the variation of base metals with pH indicates the likely interaction with ore minerals (Figure 3a). Those samples most affected by tailings (IV) have the highest base-metal concentrations (Table 2). Although the sample affected by an altered vein (V) has the lowest pH, its sum of base-metal concentrations was substantially lower than in samples affected by tailings (groups III and IV; Figure 3a). The sample with the lowest pH and base-metal sum for inflow group 4 (5,356 m) was located near the altered vein outcrop (5,295 m), and could be a mixture between the altered vein type water and water most affected by tailings. Overall, the

pattern indicates the range from unaffected to most affected inflows, and that stream sample compositions fall within the continuum.

Figure 3. Variation of (a) the sum of base metal concentrations with pH and (b) cadmium with zinc concentrations in stream and inflow samples, Animas River from Arrastra Creek to Silverton, August 2002.

Second, viewing the variation of Cd with Zn indicates a strong correlation between the two concentrations. The nearly constant slope of Cd to Zn among inflow samples (Figure 3b) suggests the weathering of sphalerite that has a relatively uniform composition from tailings and alteration zones. Although most of the increase in base metals results from the increase in Zn (Table 2), other base metals, like Cd, correlate with Zn.

The variation of Mn concentration along the study reach provides a third view of distinctions among inflow groups and also indicates the impact of tailings on stream concentrations (Figure 4). Inflows affected by tailings all had concentrations higher than the stream. The sample from 5,858 m (inflow group II) also had a high Mn concentration and was likely affected by tailings. The sample affected by the mineralized vein (inflow group V; 5,295 m) had a relatively high Mn concentration, but not nearly as high as the samples of inflow group IV (Table 2). The relatively high Mn concentrations for group III, suggest that those inflows also are affected by tailings, but, again, not to the extent as samples in group IV. The impact of individual inflows, as they may represent water entering the river is seen by the corresponding increase of instream Mn concentration.

Figure 4. Variation of dissolved, colloidal, and total (a) manganese, (b) zinc, and (c) iron concentrations with distance along the study reach, Animas River from Arrastra Creek to Silverton, August 2002 and April 2003.

Chemical Variation of the Stream Samples

Instream chemical changes occurred within the framework of inflow chemistry. That framework, as noted, is easier to define for low-flow conditions than for high-flow conditions. The chemical variation of streamwater also can be classified using cluster analysis. However, clusters of stream

groups represent sequential changes along the study reach rather than the various solute sources to the stream like the inflow clusters. The change from one group of samples to the next is indicated by patterns in Figure 4, and in subsequent figures. Each successive stream group had a higher Mn concentration, and the overall increase of Mn concentration was from about 0.2 mg/L to 1.4 mg/L at the end of the study reach. The change in Mn concentration at high flow followed the same pattern, but the increase in the final stream segment, from 7,585 m to 7,858 m, was substantially greater than during low-flow conditions.

Zn concentration was notable because it increased in most stream segments all along the study reach, and not just at the locations of specific inflows (Figure 4b). This pattern suggests the widespread contribution of the Zn from alteration, although substantial increases also occurred at the same locations along the study reach where Mn (Figure 4a) and Fe (Figure 4c) concentrations increased. The Mn to Zn mole ratio increased along the reach, particularly from 4,250 m to 5,448 m (represented by stream group II). This reach had substantial inflow of acidic springs along the right bank. The ratio increased more gradually, but consistently, along the rest of the study reach. The pattern of increasing Mn to Zn indicates the growing importance of water affected by weathering of tailings along the study reach.

For stream samples, ultrafiltration allowed the distinction of more truly dissolved concentrations from colloidal concentrations (Kimball et al., 1992; Kimball, Callender, and Axtmann, 1995). Some of the distinctions among stream groups was the result of transformations between dissolved and colloidal concentrations. Fe principally occurred in the colloidal phase along the entire study reach (Figure 4c), with the exception of one sample at 4,916 m, obtained upstream from the inflow of Boulder Creek (4,951 m). That sample may represent the cumulative effects of several acidic inflows along the left bank (Table 1), causing an increase in dissolved Fe. With the inflow of Boulder Creek, pH increased and colloidal Fe was again the dominant phase downstream. Low-flow concentration of colloidal Fe increased downstream from the inflow at 6,150 m, causing coloration of cobbles along the right bank

downstream from the inflow and subsequent seeps. During high-flow, concentration of total Fe, which was again principally the colloidal concentration, was much higher, suggesting a flush of colloidal Fe by snowmelt runoff. This flush has been measured in earlier samples from the Animas River (Church et al., 1997). Higher concentrations of colloidal Fe are important because of their capacity to sorb toxic metals and affect their transport and storage downstream (Kimball, Callender, and Axtmann, 1995; Runkel and Kimball, 2002; Schemel, Kimball, and Bencala, 2000; Smith, 1999).

Locations of Metal Loading

Locations of metal loading are best understood within this framework of inflow and stream chemistry. The detailed spatial sampling during low-flow conditions provides information about metal sources and instream changes, as well as a detailed profile of stream discharge, allowing the calculation of a mass-loading profile for each of the measured constituents, both dissolved and colloidal. The profile of mass loading quantifies the relative contribution of the many sources in a catchment, enabling decisions based on relative masses from sources. A few profiles will be used here to indicate the locations of greatest loading during low- and high-flow conditions.

Individual solutes have substantially different absolute loads so a comparison among loading patterns is facilitated by using a normalized cumulative instream load. This normalization consists of dividing the sampled instream load at each stream site by the cumulative instream load at the end of the study reach. Calculation of these quantities from a mass-loading study has been discussed elsewhere (Kimball et al., 2002; Kimball, Runkel, and Walton-Day, 2003). The normalized load varies from 0 to 1, and individual increases represent a proportion of the total loading along the study reach. Three general patterns were indicated by normalized metal-loading profiles of SO_4 , Fe, Mn, and Zn along the study reach (Figure 5a). First, loading of SO_4 is unique among the solutes because 80 percent of the loading at the A68 gage comes from sources upstream from the study reach during low flow. This reflects the loading of SO_4 and metals by sources upstream from the study reach, with the subsequent removal of the

metal load, but not the SO_4 load. Indeed, substantial loading of Mn and Zn occurred upstream from the study reach, but these metal loads are not transported all the way downstream to the study reach from Arrastra Creek to Silverton (Kimball, Walton-Day, and Runkel, 2007). Mn loading represents a second pattern that was very different from that of SO_4 loading because very little of the Mn load at the end of the study reach was from upstream sources; Mn load was attenuated upstream from the study reach (Kimball, Walton-Day, and Runkel, 2007; Paschke, Kimball, and Runkel, 2005). Within the study reach Mn loading had two very substantial increases, one from acidic springs upstream from Boulder Creek (the stream segment from 4,806 to 4,916 m), and the other at the Mayflower tailings inflow (two segments from 6,126 to 6,465 m). Mine tailings are stored at both locations. Third, patterns of Fe and Zn are similar and the loading increased consistently along the entire study reach. Over 25 percent of these loads originated upstream from the study reach (Figure 5a). Fe load increased much more than Zn load at the Mayflower tailings inflow (6,150 m).

Figure 5. Variation of normalized cumulative instream load of sulfate, iron, manganese, and zinc during (a) August 2002, low-flow conditions and (b) April 2003, high-flow conditions with distance along the study reach, Animas River from Arrastra Creek to Silverton.

Quantifying Seasonal Changes During High-Flow Conditions

Mass-loading information also aids the decision making process because it can help define seasonal variation in metal loading. Such information is critical to the process of defining total maximum daily loads (TMDL). During low flow, detail is possible because of near steady-state conditions and greater accessibility to the stream. During high flow, transient conditions prevail, and much of the sampling effort must be used to describe temporal rather than spatial changes. Usually, fewer stream and inflow sites can be accessed, and more emphasis must be placed on fewer stream sampling sites to understand the changing water quality and metal loading to the stream. These differences are illustrated here by comparing the low-flow experiment from August 2002 to the Lagrangian experiment during low-altitude snowmelt runoff in April 2003. The low-altitude runoff, in

the setting of the Animas River basin, has potential to affect metal loading because it should represent drainage from mine wastes that are away from the stream, but may not be contributing metal loads to the stream during other times of the year.

Comparing the normalized loading patterns of SO₄, Fe, Mn, and Zn between low and high flow indicates that each of these solutes had some changes in patterns (Figure 5). For SO₄ load, the loading pattern along the study reach was similar between low and high flow, but the percentage of upstream contribution during high flow (66 percent) was less than at low flow (80 percent), indicating the additional loading from the low-altitude runoff (Table 3). Upstream contributions to Mn loads were only 7 percent of the total loading at A68 for low and high flow, and indicate the importance of the study reach that contributed 93 percent of the Mn loading (Table 3). The seasonal pattern differed for Mn loading along the study reach, indicating the importance of the runoff in the last stream segment from 7,306 m to 7,858 m (39 percent of the Mn load; Figure 5b). This runoff entered the stream through a ditch that drains an area with obvious surface mining wastes near Silverton. Unlike SO₄ and Mn, the percentage of Zn load that came from sources upstream from the study reach was greater during high flow (38 percent) than low flow (28 percent). If this were from an increase of colloidal Zn, then the percentage of Fe load would have had a similar increase, but it did not (Table 3). The loading pattern of Fe was the most different between low and high flow. Upstream contribution was nearly the same for low and high flow (Table 3). During both seasons, the greatest contribution came from the Mayflower tailings inflow (percent to T5), but the percentage was substantially greater during high flow at 52 percent compared to 36 percent. This greater contribution could result from re-suspension of colloidal Fe that had been deposited on the streambed during low-flow conditions or from greater ground-water contribution from the Mayflower tailings piles during snowmelt.

Table 3. Comparison of low- and high-flow loading and concentrations, Animas River from Arrastra Creek to Silverton, August 2002 and April 2003.

Even though the absolute values of load were substantially greater during high flow than during low flow, the corresponding concentrations were almost equal (Table 3; concentrations at T7). Because of the decrease in hardness due to dilution of concentrations of Ca and Mg during high flow conditions, the toxicity criteria are lower, and the greater loading during snowmelt runoff does not result in increased toxicity. Considering all these changes, the comparison between low and high flow loading can provide important information for making decisions, even though the spatial detail is much less than for the high-flow study.

The April 2003 study included samples from 6 sites equipped with auto-samplers. These samples indicated temporally variability of sources along the study reach during the low-altitude snowmelt runoff and also changes resulting from biogeochemical processes over time (Figure 6). Distinguishing between these two kinds of variation is facilitated by considering the changes in loads with time. Temporal variation in loads of SO₄ (Figure 6a) and Mn (Figure 6b) both reflect variability in sources of loading to the stream, but their patterns indicate important differences. Loading of SO₄ increased from site to site, and the magnitude of that increase varied with time. This clearly indicates the diel effect of snowmelt runoff during the day, particularly for the segment between sites T6 and T7. The increase in SO₄ load was greatest at site T7 during the period of runoff from 14:00 to 17:00 hours on 4/16/03, and again between 10:38 and 12:45 on 4/17/03. Chemical analyses of the transient samples are listed in table S2 (located with supplemental material).

Figure 6. Variation of (a) sulfate, (b) manganese, and (c) zinc loads with time, Animas River from Arrastra Creek to Silverton, April 2003.

Table S2. Chemical analyses of samples from auto-samplers during high-flow conditions, Animas River from Arrastra Gulch to Silverton, April 2003.

The increase of Mn load was apparent from site to site, but, unlike to that of SO₄, the diel variation was minimal, except for the change between sites T6 and T7. The diel increase of both SO₄ and Mn loads between sites T6 and T7 was the result of drainage from the inflow at 7,750 m. In general,

diel variation at sites T1 through T6 was minimal, but site to site loading was substantial, particularly between sites T4 and T5. This Mn loading pattern, in contrast to that of SO₄, suggests that this temporal sampling represents constant sources that were diluted by the increased streamflow, retaining the nearly constant load. This pattern is consistent with ground-water sources of Mn loading rather than snowmelt runoff (again, with the exception of the segment from T6 to T7). It is plausible that SO₄ is more prone to diel variation than Mn because SO₄ is more likely a part of soluble salts that might be washed into the stream. However, such salts would not be abundant in early spring. These distinctions can be important in making decisions about remediation and achieving TMDL goals.

Quantifying Environmental Processes

The temporally detailed sampling during the low-altitude snowmelt runoff provided data to evaluate biogeochemical processes that affect instream concentrations. Over the period of high-flow synoptic sampling, when snowmelt runoff occurred, Zn load decreased (Figure 6c). This is in contrast to loads of SO₄ and Mn that increased (Figure 6a and b). Subsequently, from about 19:00 to 23:00 hours on 4/16/03 Zn load increased. Because this is a pattern of loading rather than concentration, the decrease indicates a reactive loss of Zn, and not just a decrease through dilution. Diel variation of Zn concentration in this stream was between 0.28 and 0.73 mg/L, more than doubling in concentration. A monitoring data set that did not account for this kind of diel variation, could not accomplish its purposes.

The Zn pattern does not correspond with the Mn that was diluted by the increase in snowmelt runoff. Sorption is the most likely reactive processes that could remove Zn from solution during the hours of synoptic sampling. The increase of colloidal Fe load increased during the snowmelt runoff (note change in high-flow synoptic load, Figure 5), and could have increased the likelihood of Zn sorption. This diel process for Zn in near-neutral waters has been documented in other streams affected by mine drainage during low-flow conditions (Gammons et al., 2005; Nimick et al., 2003; Nimick,

Cleasby, and McCleskey, 2005). After the loading of Zn increased late in the day, it decreased during the morning hours the next day. This pattern indicates that Zn variation was independent from the dilution by snowmelt runoff. The timing of the diel increase in metals is consistent with the results of previous studies (Nimick et al., 2003). This temporal process should influence sampling designs for monitoring, as suggested by Nimick et al. (2003).

A mass-loading approach provides information that is helpful in making decisions about remediation of the effects of mine drainage. Having the right information can result in cost-effective decisions that may provide the greatest improvements to the stream. Remediation decisions must be based on an understanding of the sources of metal loading, seasonal changes of loading, and reactive processes that affect loading. Three field-scale experiments on the Animas River illustrate the kinds of information that can support remediation decisions. A spatially-detailed, synoptic sampling during low-flow conditions provided a guide to the locations where metal loading occurred. A Lagrangian experiment during high-flow conditions indicated the significance of seasonal variability. A temporally detailed experiment indicated the importance of diel processes to guide the design of monitoring programs. Bringing all of this information together can be important in the planning and implementation of a TMDL process for streams affected by mine drainage.

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Table 1. Description of synoptic sampling sites, Animas River, Colorado

Downstream distance, in meters	Source	Low flow	High flow	Description	Low-flow discharge, in L/s	High-flow discharge, in L/s	Low-flow bromide, in mg/L	High-flow bromide, in mg/L	Group	pH, in standard units
3,655	S	LF		Injection site and T0 upstream from injection	620		.05		1	7.77
3,909	S	LF	HF	Downstream from injection at right bank stand of young spruce	620	1,461	1.22	1.11	1	7.88
4,033	RBI	LF	HF	Right-bank cascade from rocky bank	1.00	39	.05		1	8.32
4,166	S	LF	HF	T1 site - Upstream from Arastra Gulch	621	1,500	1.22	1.13	1	8.10
4,186	LBI	LF	HF	Arastra Gulch	70.9		.05		1	8.05
4,250	S	LF	HF	T2 site - Downstream from Arastra Gulch	692	1,515	1.10	1.09	2	7.95
4,300	RBI	LF		Small spring upstream from pipe bridge			.06		2	7.33
4,353	RBI	LF		Stream level spring			.49		3	4.48
4,385	RBI		HF	Moss and Al pptn at spring	.75					
4,473	S	LF		Downstream from right bank acid inflows	720		1.06		2	7.91
4,520	RBI	LF		Additional spring on right bank	.10		.05		3	4.73
4,533	RBI		HF	Marshy ponds with algae near manganese	.75					
4,544	RBI	LF		Algal pond downstream from dry marsh	.10		.05		3	5.05
4,581	S	LF		Upstream from dry inflow draining left bank and old gravity mill	720		1.04		2	8.03
4,586	RBI		HF	Ponded water right bank; dripping from overhanging bankank	.75					
4,713	S	LF		Downstream from "Pinicle Gap"	727		1.05		2	7.99
4,806	S	LF		Upstream from Acid inflows	735		1.04		2	7.74
4,886	RBI		HF	Seep w/ acid algae	.75					
4,916	S	LF		T2/T3 --> Downstream from acid inflows	735	1,558	1.05	1.06	2	7.83
4,951	RBI	LF	HF	Boulder Creek A62	31.4	.90	.05		1	8.07
5,016	S	LF		Downstream from Boulder Creek	766		1.00		2	7.90
5,038	RBI	LF	HF	Substantial orange precipitate in inflow	4.05	.04	.05		4	6.14
5,131	S	LF		Downstream from orange precipitate tailings bin	770		.97		2	7.79
5,161	LBI	LF		Pond to stream left bank with fish			.05		2	7.02
5,221	LBI	LF	HF	Drainage from Aspen Mine			.02	.05	2	7.52
5,251	S	LF		Downstream from Aspen Mine inflow	774		.99		2	7.84
5,295	LBI	LF		Drainage from left bank alteration	6.13		.05		5	2.42
5,306	S	LF		Downstream from seeps on both sides	781		1.01		3	7.81
5,356	RBI	LF	HF	Discharge from slough draining tailings	15.8	.04	.05		3	3.67
5,448	S	LF		Integrating right bank inflow from slough	796		.96		3	7.89
5,536	S	LF	HF	T4 --> Stream at Power Plant	797	1,649	.96	.99	3	7.89
5,756	S	LF		Upstream from right bank drainage ditch behind power plant	798		.94		3	7.79
5,858	RBI	LF	HF	Seep along 60 m of grass	.95	.00	1.44		2	6.19
5,965	S	LF		Small pool near stream	.24		.05		2	6.71
6,038	S	LF		Old T5--Integration of seeps on both sides	799		.95		3	7.78
6,126	S	LF		Upstream from substantial right bank staining	799		.98		3	7.66
6,131	LBI	LF		At base of colluvium			.11		2	6.88
6,150	RBI	LF	HF	Red stained right bank discharge			.05		3	5.46
6,265	S	LF		Downstream from major right bank inflow from tailings drainage	800		.96		4	7.79
6,465	S	LF		Downstream from many right bank seeps	801		.95		4	7.64
6,745	S	LF	HF	T5 --> At Lacawana Bridge	802	1,701	.95	.96	4	7.56
6,994	S	LF		Upstream from Lacawana Mill	803		.98		4	7.57

Table 1. Description of synoptic sampling sites, Animas River, Colorado

Downstream distance, in meters	Source	Low flow	High flow	Description	Low-flow discharge, in L/s	High-flow discharge, in L/s	Low-flow bromide, in mg/L	High-flow bromide, in mg/L	Group	pH, in standard units
7,049	RBI	LF		New right-bank inflow	.78		.05		4	5.79
7,177	S	LF		Upstream from Lacawana discharge, or Swansea G.?	804		.94		4	7.41
7,201	LBI	LF		Discharge from Lacawana area, pond	.55		.05		1	7.95
7,201	RBI		HF	Drains right bank "protected" wetland area						
7,306	S	LF	HF	T6 --> Downstream from Lacawana Mill (A66)	804	1,759	.95	.95		
7,585	S	LF		Downstream from braids, good mixing	805		.95		4	7.64
7,750	RBI	LF	HF	Ditch draining from pond nr roaster fines?	1.17	805	.17	.05	4	5.97
7,858	S	LF	HF	T7/T3--At bridge / gage A68	807	1,808	.94	.90	4	7.39

Table 2 Chemical composition of samples representing inflow groups determined by cluster analysis, Animas River, August 2002.

[Group. Group from cluster analysis; Distance, in meters along study reach, pH, in standard units; Ficklin, sum of base metal concentrations; Ca, calcium; Mg, magnesium; SO₄, sulfate; Alk, alkalinity as calcium carbonate; Al, aluminum; Cd, cadmium; Cu, copper; Fe, iron; Mn, manganese; Zn, zinc; all concentrations in milligrams per liter]

Group	Extent of interaction with mine wastes	Representative sample	pH	Ficklin	Ca	Mg	SO ₄	Alk	Al	Cd	Cu	Fe	Mn	Zn
I	Unaffected	A3-4186	8.05	.18	41.5	1.97	66.7	51.9	.02	.0014	.0056	.004	.0012	.17
II	Slightly affected	A3-6131	6.88	.51	121	2.98	315	30.8	.06	.0013	.0018	.05	.13	.50
III	Moderately affected	A3-7750	5.97	7.94	398	27.2	1,217	14.0	.61	.0413	.0452	.27	75.1	7.82
IV	Most affected	A3-4544	5.05	71.0	268	52.4	2,179	<.01	16.4	.2886	.6982	.05	575	69.8
V	Affected by alteration vein	A3-5295	2.42	4.29	59.8	13.1	1,009	<.01	21.2	.0118	.6919	163	7.28	2.96

Table 3. Comparison of loading during low and high flow conditions
[kg/day, kilograms per day; mg/L, milligrams per liter]

	Sulfate		Manganese		Zinc		Iron	
	Low	High	Low	High	Low	High	Low	High
Start of reach, kg/day	6,486	12,241	10.4	23.2	10.7	39.1	2.78	11.0
End of reach, kg/day	8,097	18,481	141	315	38.5	103	8.30	36.6
Net gain, kg/day	1,611	6,240	131	292	27.8	63.5	5.52	25.6
Total gain, kg/day	8,097	18,481	141	315	38.5	103	8.30	36.6
Concentration at T7, mg/L	119	118	1.39	1.90	0.61	0.61	0.002	0.002
Percent from reach	20%	34%	93%	93%	72%	62%	67%	70%
Percent to T1 (upstream)	80%	66%	7%	7%	28%	38%	33%	30%
Percent to T3	9%	5%	31%	21%	15%	24%	10%	0%
Percent to T4	8%	7%	19%	9%	19%	0%	16%	0%
Percent to T5	0%	7%	24%	23%	16%	27%	36%	52%
Percent to T6	3%	3%	10%	0%	21%	11%	2%	1%
Percent to T7	0%	12%	8%	39%	0%	0%	4%	17%











